Short communication

Effect of L-arginine on the catalytic activity and stability of nickel nanoparticles for hydrolytic dehydrogenation of ammonia borane

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HIGHLIGHTS

► Amorphous Ni catalysts were synthesized in an aqueous $NaBH_4$/NH_3BH_3 solution.
► We study the effect of addition of L-arginine in the synthesis process.
► Ni species aggregate after cycle tests for NH_3BH_3 hydrolysis without L-arginine.
► Ni particles with L-arginine show high dispersion and activity for the cycle tests.

ARTICLE INFO

ABSTRACT

Amorphous nickel catalysts were synthesized by reducing the nickel(II) species in an aqueous $NaBH_4$/NH_3BH_3 solution with and without L-arginine. The nickel catalyst with L-arginine maintains relatively high activity for hydrolysis of NH_3BH_3 to generate a stoichiometric amount of hydrogen with the cycle number up to 11 (827 mL s^{-1} (mol-Ni)$^{-1}$ at the 11th cycle with L-arginine = 35 mg), while the reaction rate in the presence of the bare nickel catalyst was relatively low through the cycle number up to 11 (232 mL s^{-1} (mol-Ni)$^{-1}$ at the 11th cycle). After catalytic reaction, the nickel catalyst with L-arginine possesses the high dispersion (diameters of nickel nanoparticles <5 nm), while the agglomerate of nickel in the bare nickel catalyst is observed. The results indicate that L-arginine maintains the dispersion of nickel nanoparticles (diameters of nickel nanoparticles <10 nm), leading to higher activity against cycle tests than the bare nickel catalyst.

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1. Introduction

There have been intensive efforts for developing safe and efficient methods for hydrogen storage, a key issue of the hydrogen economy [1–3]. Ammonia borane (NH_3BH_3) possesses a low molecular weight (30.9 g mol^{-1}) and high hydrogen content (19.6 wt%) [4] and therefore makes it an attractive candidate for chemical hydrogen storage application [5–20]. NH_3BH_3 is nontoxic, stable, and environmentally benign, can be handled at room temperature and can release hydrogen gas upon catalytic hydrolysis under mild conditions (Eq. (1)) [4]. The hydrolysis occurs at appreciable rate in the presence of a suitable acid or a suitable catalyst at ambient temperature [8–15]. For the viewpoint of practical application, the development of efficient, low-cost, and stable catalysts to further improve the kinetic properties under moderate conditions is therefore very important [8–20]. Nowadays, there is a general interest in searching for more abundant first-row transition-metal-based catalysts, such as Fe, Co, Ni, and so on, to catalyze the hydrolysis of NH_3BH_3 with high efficiency [21–29]. However, the success in their application highly depends on the stability of the nanoparticles because of their high tendency to form agglomerates and their extreme reactivity toward water and oxygen [30–33].

A general solution to stabilize or protect the metal nanoparticles is to protect them with some outer materials including the precious metals [34], silica [35–38], zeolite [39,40], transition-metal oxides [41], carbon [42], and organic compounds such as polymers [43–55]. Among these protecting materials, the organic compounds have the relatively weak binding interaction with the nanoparticles which is vital for the catalytic application where surface catalytically active sites are urgently needed [56–58]. However, those metallic nanoparticles dispersed in the solution of polymeric materials are commonly not air stable [30]. Moreover,

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most of the preparation procedures reported to date rely heavily on organic solvents (not an aqueous phase, mainly because of the hydrophobicity of the capping agent used), expensive and/or toxic organometallic compounds (metal precursors), and synthetic macromolecules (capping and/or dispersing agents), as well as high temperature and high dilution conditions [43,45,46], and thus inevitably resulting in high production cost and serious environmental issues while addressing industrial production. Therefore, finding suitable and effective protection agents to maintain and exert the potent catalytic ability of metal nanoparticles in aqueous solution or even in air is still a challenge to be faced. Starch [50], poly(N-vinyl-2-pyrrolidone) (PVP) [51], laurate [48,53], poly(4-styrenesulfonic acid-co-maleic acid) (PSSA-co-MA) [52,55] have been successfully applied as dispersing and stabilizing agents for metal nanoparticles for hydrolysis of ammonia borane.

Herein, we first apply L-arginine, which is one of amino acids that have been used for stabilizing quantum dots such as CdS [59], as the dispersing agent for the facile synthesis of Ni nanoparticles in aqueous solution in air (water/air) at room temperature. The present method completely avoids the use of volatile organic solvents, expensive organometallic precursors, and synthetic macromolecules. The Ni nanoparticles as synthesized possess high catalytic activity and stability against cycle tests for hydrolysis of NH_3BH_3 for chemical hydrogen storage at room temperature.

2. Experimental

2.1. Experimental procedures for synthesis of nickel catalysts and hydrolysis of ammonia borane

A mixture of sodium borohydride (NaBH$_4$, 7.0 mg (1.9×10^{-4} mol), Aldrich, >98.5%) and ammonia borane (NH$_3$BH$_3$, 45 mg (1.3×10^{-3} mol), Aldrich, 90%) was kept in a two-necked round-bottom flask. One neck was connected to a gas burette, and the other was fitted with a septum inlet to introduce 5 mL of aqueous nickel chloride hexahydrate (NiCl$_2$·6H$_2$O, 31.2 mg (1.3×10^{-4} mol), Kanto Chem. Co., >98%) solution mixed with L-arginine (0, 12, 23, 35 mg (0, 0.7, 1.3, 2.0×10^{-4} mol, respectively), Acros Organics, >98%). The reaction started when the solution was syringed to the mixture of NaBH$_4$ and NH$_3$BH$_3$, and the evolution of gas was monitored using the gas burette. The reactions were carried out at room temperature in air. For cycle tests, additional equivalents of aqueous NH$_3$BH$_3$ solution (0.26 M, 5 mL) were added into the reaction flask after the hydrogen generation reaction was completed. The evolution of gas was monitored using the gas burette. Such cycle tests of the catalyst for the hydrolysis of NH$_3$BH$_3$ were carried out eight times in air.

The samples after hydrolysis of NH$_3$BH$_3$ were separated from the reaction solution by centrifugation, dried in desiccators, and then used for characterization.

2.2. Characterization

The morphologies of the bare nickel catalyst and the L-arginine stabilized catalyst were observed using a Hitachi FE2000 transmission electron microscope (TEM) operating at an acceleration voltage of 200 kV. Samples for the measurements were prepared by placing a drop of a colloidal dispersion of a centrifuged sample diluted in ethyl alcohol and ultrasonicated for 5 min onto a carbon-coated copper grid.

UV−vis electronic absorption spectra were recorded on an UV-2500 (Shimadzu) UV−vis spectrophotometer. A quartz cell with a path length of 1 cm was used and spectra were collected over the range of 300−800 nm.

The samples were used for the FTIR analysis. FTIR spectra of both L-arginine and the L-arginine-stabilized nickel nanoparticles were recorded using a PerkinElmer Fourier transform infrared spectro-photometer (FTIR) with a resolution of 4 cm^{-1} in the angle attenuated total reflectance (ATR) sampling mode. The sample powder was placed on the horizontal face of the internal reflectance crystal where total internal reflection occurs. The zinc selenide (ZnSe) crystal with a transmission range of 4000−650 cm^{-1} was used in this experiment.

3. Results and discussion

The water dispersible L-arginine stabilized Ni nanoparticles were prepared from the reduction of aqueous NiCl$_2$ solution by NaBH$_4$/NH$_3$BH$_3$ in the presence of L-arginine at room temperature. Fig. 1 shows time courses of the hydrogen evolution from aqueous solutions of NaBH$_4$ and NH$_3$BH$_3$ mixtures during the preparation of Ni catalysts without or with L-arginine in air. The evolutions of 98 mL of hydrogen were finished in 13 and 10 min in the presence of NiCl$_2$ (Fig. 1a) and in the presence of NiCl$_2$ with L-arginine (Fig. 1b), respectively (NH$_3$BH$_3$/NiCl$_2$/NaBH$_4$ = 1.0/0.10/0.15). There is no hydrogen evolution from the aqueous NH$_3$BH$_3$ solution without NaBH$_4$ in the presence of NiCl$_2$ with L-arginine. The result suggests that NaBH$_4$ is necessary for reducing Ni^{2+} via reaction (1).

$$4Ni^{2+} + BH_4^- + 2H_2O \rightarrow 4Ni + BO_2^- + 8H^+ \tag{1}$$

The effect of NaBH$_4$ has been reported for the Fe- [8], Ni-[50,51,55], and Co- [55] catalyzed hydrolysis of NH$_3$BH$_3$. In the present reaction system, NaBH$_4$ was mixed with H$_2$O, NH$_3$BH$_3$, and the catalyst precursor. Hydrogen is evolved via the following two reactions besides reaction (1):

$$NaBH_4 + 2H_2O \rightarrow Na^+ + BO_2^- + 4H_2 \tag{2}$$

$$NH_3BH_3 + 2H_2O \rightarrow NH_4^+ + BO_2^- + 3H_2 \tag{3}$$
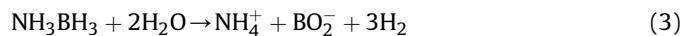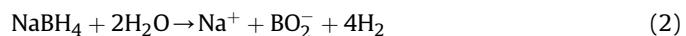
Under the present reaction condition, about 6 mL of hydrogen (2.4×10^{-4} mol) is generated via reaction (2) from residual amount of NaBH$_4$ consumed via the reaction (1) (1.9×10^{-4}(total amount of NaBH$_4$)-1.3×10^{-4} (amount of NaBH$_4$ consumed via the reaction (1)) = 0.6×10^{-4} mol), and about 92 mL of hydrogen (3.7×10^{-3} mol) is generated via reaction (3), experimentally. The molar ratios of the hydrolytically generated hydrogen to the initial NH$_3$BH$_3$ both in the presence of the bare Ni catalyst and in the
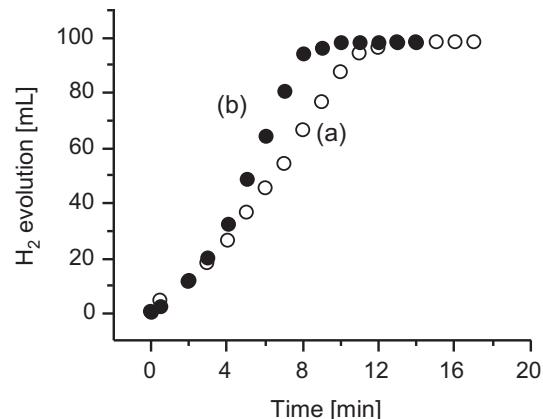

Fig. 1. Hydrogen generation from hydrolysis of ammonia borane (0.26 M, 5 mL) with NaBH$_4$ in the presence of (a) the Ni bare catalyst and (b) the L-arginine stabilized Ni catalyst (L-arginine = 35 mg) at room temperature in air (Ni/NH$_3$BH$_3$ = 0.10).
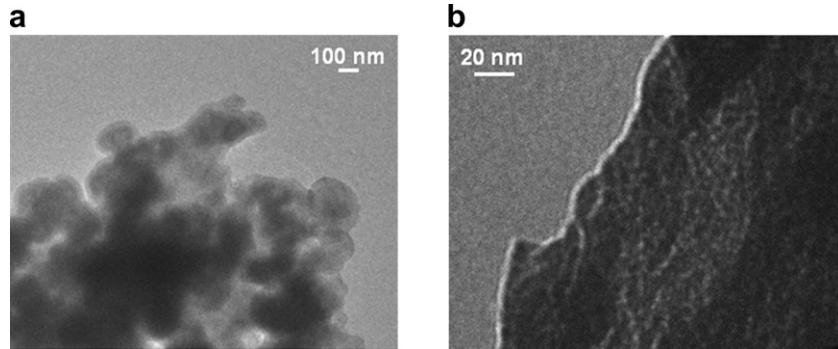
Fig. 2. TEM images of in-situ synthesized (a) bare Ni catalyst and (b) L-arginine stabilized Ni catalyst (L-arginine = 35 mg).
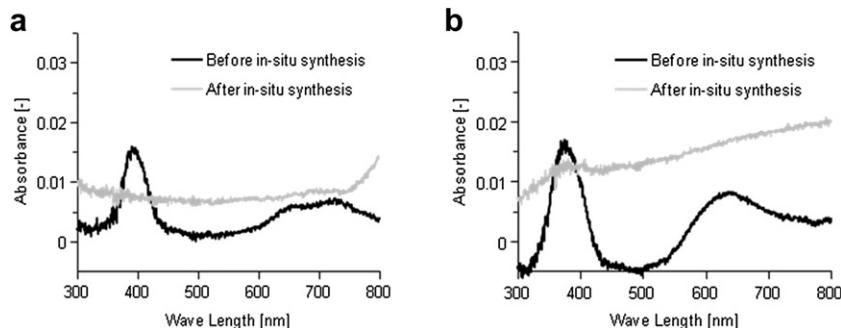

Fig. 3. UV–vis spectra of (a) the bare Ni catalyst and (b) L-arginine stabilized Ni catalyst (L-arginine = 35 mg) before and after in-situ synthesis.
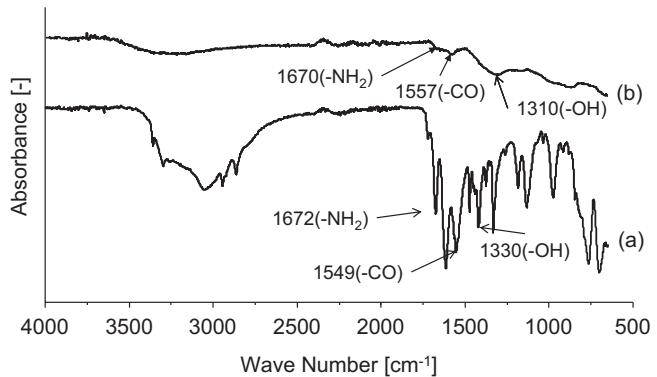

Fig. 4. ATR-FTIR spectra of L-arginine and L-arginine stabilized Ni catalyst (L-arginine = 35 mg).

presence of the L-arginine stabilized Ni catalyst are 2.9, very close to the theoretical value of 3.0 [14,50,51,55]. These results indicate that the hydrolysis of NH_3BH_3 is almost completed in the presence of the bare Ni catalyst and in the presence of the L-arginine stabilized Ni catalyst.

The morphologies of the bare Ni catalyst and the L-arginine stabilized Ni catalyst after the preparation in the aqueous solutions of $NaBH_4$ and NH_3BH_3 mixtures were examined by TEM measurements. The TEM images of the bare Ni catalyst reveal that the catalyst contains grains with an amorphous structure. The result indicates that the Ni nanoparticles formed by $NaBH_4/NH_3BH_3$ reduction of $NiCl_2$ readily agglomerate ultimately to the bulk metal precipitating out of the solution without adding L-arginine in aqueous solution. The TEM images of the L-arginine stabilized Ni catalyst reveal that the catalyst contains particles with diameters of
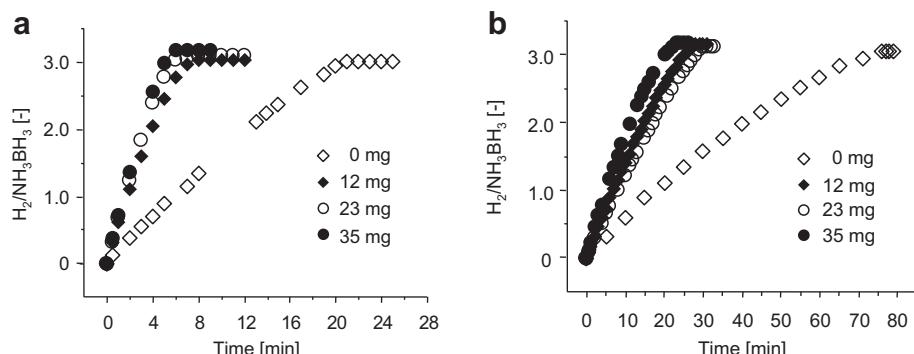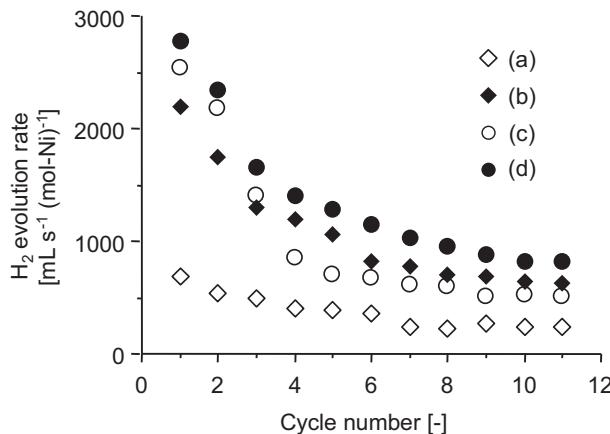

Fig. 5. Hydrogen generation from the hydrolysis of NH_3BH_3 catalyzed by the Ni catalysts with the different amount of L-arginine (0, 12, 23, 35 mg) at (a) the 1st cycle and (b) the 11th cycle. $Ni/NH_3BH_3 = 0.10$ (at each cycle) at room temperature in air.

Fig. 6. Hydrogen evolution rates for the uninterrupted cycle of Ni catalyst with L-arginine = (a) 0, (b) 12, (c) 23, (d) 35 mg vs. the cycle number at room temperature in air (Ni/NH$_3$BH$_3$ = 0.10 at each cycle).

less than 5 nm (Fig. 2), indicating that L-arginine can be used to synthesize well-dispersed Ni nanoparticles.

L-arginine stabilized Ni nanoparticles were characterized by using UV−vis and FTIR spectroscopic methods. The formation of L-arginine stabilized Ni nanoparticles could be followed by monitoring the UV−vis electronic absorption spectra as shown in Fig. 3. The starting solution of NiCl$_2$ shows an absorption band at about 400 nm, which disappears when all of the Ni^{2+} are completely reduced to metallic Ni in both the bare Ni catalyst and the L-arginine stabilized Ni catalyst [55,56,58]. Fig. 4(a) presents the FTIR spectra of pure L-arginine and the L-arginine stabilized Ni nanoparticles. Compared with the spectra of pure L-arginine, the out-of-plane bending band of NH$_2$ at 1682 cm^{-1}, the stretching bending band of CO at 1562 cm^{-1}, and the bending band of OH at 1330 cm^{-1} in L-arginine appear at 1651, 1574 and 1372 cm^{-1} in L-arginine stabilized Ni nanoparticles, respectively [60]. However, the intensities of all the three bands decrease obviously. From these results, on the one hand, there is a trace amount of L-arginine in the L-arginine stabilized Ni nanoparticles. On the other hand, there are certain interactions between the L-arginine stabilized Ni nanoparticles and the functional groups of the L-arginine, including NH$_2$, CO, and OH. These interactions may contribute to the formation and the stabilization of the L-arginine stabilized Ni nanoparticles.

Fig. 5 shows time courses of the hydrogen evolution from aqueous NH$_3$BH$_3$ solutions catalyzed by Ni catalysts with various amounts of L-arginine (0−35 mg) at the 1st and 11th cycle in air, respectively. The amount of hydrogen evolution does not depend on the amount of L-arginine, while the evolution rate significantly depends on the amount of L-arginine. At the 1st cycle, a stoichiometric amount of hydrogen was evolved in 21, 8, 8, and 6 min in the presence of the bare Ni catalyst and in the presence of the L-arginine stabilized Ni catalysts with L-arginine 0, 12, 23, and 35 mg, respectively. The results indicate that the L-arginine stabilized Ni catalysts show higher hydrogen evolution rates than the bare Ni catalyst. At the 11th cycle, hydrogen evolution was finished in 76, 28, 30 and 23 min in the presence of the bare Ni catalyst and in the presence of the L-arginine stabilized Ni catalysts with L-arginine = 0, 12, 23, and 35 mg, respectively. The results in Fig. 4a and b indicate that the hydrogen evolution rates are maintained in the presence of the L-arginine stabilized Ni catalysts with 12, 23 and 35 mg, while the hydrogen evolution rates decrease in the presence of the bare Ni catalyst. Fig. 6 shows the hydrogen evolution rates for the uninterrupted cycle of Ni catalysts. The evolution rates were calculated by averaging the hydrogen amounts evolved every minute in the range 5−50% of the maximum amounts evolved in the presence of each catalyst. At the 1st cycle, the L-arginine stabilized Ni catalysts with L-arginine = 12, 23 and 35 mg show higher hydrogen evolution rates than the bare Ni catalyst. The evolution rates in the presence of the L-arginine stabilized Ni catalyst with L-arginine = 12, 23 and 35 mg are 3.2, 3.7 and 4.1 times, respectively, higher than that in the presence of the bare Ni catalyst. At the 11th cycle, the hydrogen evolution rates over the L-arginine stabilized Ni catalysts with L-arginine = 12, 23 and 35 mg are still higher hydrogen evolution rates than the bare Ni catalyst. The evolution rates in the presence of the L-arginine stabilized Ni catalyst with L-arginine = 12, 23 and 35 mg are 2.7, 2.2 and 3.6 times, respectively, higher than that in the presence of the bare Ni catalyst. The results indicate that L-arginine is an effective stabilizer to improve the activity of the Ni catalyst on cycle tests in [L-arginine]/[Ni] ratio less than 1.5.

The morphologies of the bare Ni catalyst and the L-arginine stabilized Ni catalyst after catalytic reaction were examined by TEM measurements. The TEM images of the bare Ni catalyst reveal that the catalyst contains aggregates (Fig. 7a). These results indicate that amorphous nickel in the bare Ni catalyst agglomerates during the reaction. The TEM images of the L-arginine stabilized Ni catalyst reveal that the catalyst contains particles with diameters of less than 10 nm (Fig. 7b). As shown in Fig. 2b, the L-arginine stabilized Ni catalyst also contains an amorphous structure after the hydrolysis of the NaBH$_4$ and NH$_3$BH$_3$ mixture. The results indicate that agglomeration of nickel during the reaction can be prevented by the existence of L-arginine.
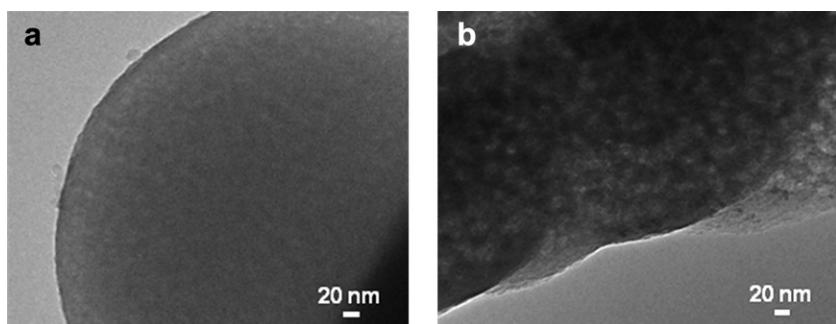
Fig. 7. TEM images of (a) the bare Ni catalyst and (b) the L-arginine stabilized Ni catalyst (L-arginine = 35 mg) after catalytic reaction.

4. Conclusion

An amorphous nickel catalyst stabilized by L-arginine was synthesized by reducing the nickel(II) species in an aqueous solution of $NaBH_4$ and NH_3BH_3 mixture, and nickel nanoparticles with diameters of less than 5 nm are identified in the L-arginine stabilized nickel catalyst while grains with an amorphous structure are identified both in the bare nickel catalyst by TEM measurements. The L-arginine stabilized nickel catalyst exhibits almost the same activity for the hydrolysis of NH_3BH_3 to generate almost a stoichiometric amount of hydrogen as the bare nickel catalyst. However, the L-arginine stabilized nickel catalyst shows higher durability than the bare nickel catalyst. Agglomeration of amorphous nickel is observed for the bare nickel catalyst, whereas the L-arginine stabilized nickel catalyst maintains the particle size with the diameters of less than 10 nm after catalytic reaction. The results indicate that L-arginine prevents agglomeration of amorphous nickel, resulting in high durability.

Acknowledgements

References

[1] Basic Research Needs for the Hydrogen Economy, Report of the Basic Energy Sciences Workshop on Hydrogen Production, Storage and Use, 13–15 May 2003, Office of Science, U.S. Department of Energy. www.sc.doe.gov/bes/hydrogen.pdf.
[2] J. Turner, G. Sverdrup, K. Mann, P.G. Maness, B. Kroposki, M. Ghirardi, Int. J. Energy Res. 32 (5) (2008) 379–407.
[3] A.W.C.V. Berg, C.O. Arean, Chem. Commun. (2008) 668–681.
[4] Basic Research Needs Catalysis for Energy, Report from the U.S. Department of Energy, Basic Energy Sciences Workshop Report, 6–8 August 2007. <http://www.sc.doe.gov/bes/reports/list.html>.
[5] A. Gutowska, L.Y. Li, Y.S. Shin, C.M.M. Wang, X.H.S. Li, J.C. Linehan, R.S. Smith, B.D. Schmid, W. Shaw, M. Gutowski, T. Autrey, Angew. Chem., Int. Ed. 44 (23) (2005) 3578–3582.
[6] Y.S. Chen, J.L. Fulton, J.C. Linehan, T. Autrey, J. Am. Chem. Soc. 127 (10) (2005) 3254–3255.
[7] V. Sit, R.A. Geanangel, W.W. Wendlandt, Thermochim. Acta 113 (1987) 379–382.
[8] J.-M. Yan, X.-B. Zhang, S. Han, H. Shioyama, Q. Xu, Angew. Chem., Int. Ed. 47 (12) (2008) 2287–2289.
[9] M. Chandra, Q. Xu, J. Power Sources 168 (1) (2007) 135–142.
[10] A. Paul, C.B. Musgrave, Angew. Chem., Int. Ed. 46 (43) (2007) 8153–8156.
[11] C.W. Yoon, L.G. Sneddon, J. Am. Chem. Soc. 128 (43) (2006) 13992–13993.
[12] M. Chandra, Q. Xu, J. Power Sources 156 (2) (2006) 190–194.
[13] M. Chandra, Q. Xu, J. Power Sources 159 (2) (2006) 855–860.
[14] Q. Xu, M. Chandra, J. Power Sources 163 (1) (2006) 364–370.
[15] C.A. Jaska, K. Temple, A.J. Lough, I. Manners, Chem. Commun. 11 (2001) 962–963.
[16] F.H. Stephens, V. Pons, R.T. Baker, Dalton Trans. (2007) 2613–2626.
[17] F.H. Stephens, R. Baker, M.H. Matus, D.J. Grant, D.A. Dixon, Angew. Chem., Int. Ed. 46 (5) (2007) 746–749.
[18] R.J. Keaton, J.M. Blacquiere, R.T. Baker, J. Am. Chem. Soc. 129 (7) (2007) 1844–1845.
[19] M.C. Denney, V. Pons, T.J. Hebden, D.M. Heinekey, K.I. Goldberg, J. Am. Chem. Soc. 128 (37) (2006) 12048–12049.
[20] M.E. Bluhm, M.G. Bradley, R. Butterick III, U. Kusari, L.G. Sneddon, J. Am. Chem. Soc. 128 (24) (2006) 7748–7749.
[21] M. Kawamura, K. Sato, Chem. Commun. (2006) 4718–4719.
[22] C.H. Jun, Y.J. Park, Y.R. Yeon, J. Choi, W. Lee, S. Ko, J. Cheon, Chem. Commun. (2006) 1619–1621.
[23] A. Hu, G.T. Yee, W. Lin, J. Am. Chem. Soc. 127 (36) (2005) 12486–12487.
[24] R.D. Ambashta, S. Mohammad Yusuf, M.D. Mukadam, S. Singh, P. Kishan Wattal, D. Bahadur, J. Magn. Magn. Mater. 293 (1) (2005) 8–14.
[25] A.H. Lu, W. Schmidt, N. Matoussevitch, H. Bönnemann, B. Spliethoff, B. Tesche, E. Bill, W. Kiefer, F. Schüth, Angew. Chem., Int. Ed. 43 (33) (2004) 4303–4306.
[26] X. Gao, K.M.K. Yu, K.Y. Tam, S.C. Tsang, Chem. Commun. (2003) 2998–2999.
[27] R. Hirsch, E. Katz, I. Willner, J. Am. Chem. Soc. 122 (48) (2000) 12053–12054.
[28] S.B. Kalidindi, M. Indirani, B.R. Jagirdar, Inorg. Chem. 47 (16) (2008) 7424–7429.
[29] S.B. Kalidindi, U. Sanyal, B.R. Jagirdar, Phys. Chem. Chem. Phys. 10 (38) (2008) 5870–5874.
[30] A.H. Lu, E.L. Salabas, F. Schüth, Angew. Chem., Int. Ed. 46 (8) (2007) 1222–1244.
[31] R.N. Grass, E.K. Athanassiou, W.J. Stark, Angew. Chem., Int. Ed. 46 (26) (2007) 4909–4912.
[32] J. Dobson, Gene Ther. 13 (4) (2006) 283–287.
[33] D.L. Huber, Small 1 (5) (2005) 482–501.
[34] J.I. Park, J. Cheon, J. Am. Chem. Soc. 123 (24) (2001) 5743–5746.
[35] T. Sen, A. Sebastianelli, I.J. Bruce, J. Am. Chem. Soc. 128 (22) (2006) 7130–7131.
[36] T. Umegaki, J.-M. Yan, X.-B. Zhang, H. Shioyama, N. Kuriyama, Q. Xu, J. Power Sources 191 (2) (2009) 209–216.
[37] H.-L. Jiang, T. Umegaki, T. Akita, X.-B. Zhang, M. Haruta, Q. Xu, Chem.—Eur. J. 16 (10) (2010) 3132–3137.
[38] T. Umegaki, J.-M. Yan, X.-B. Zhang, H. Shioyama, N. Kuriyama, Q. Xu, J. Power Sources 195 (24) (2010) 8209–8214.
[39] M. Zahmakıran, S. Özkar, Appl. Catal., B: Environ 89 (1–2) (2009) 104–110.
[40] M. Rakap, S. Özkar, Int. J. Hydrogen Energy 35 (8) (2010) 3341–3346.
[41] I.S. Lee, N. Lee, J. Park, B.H. Kim, Y.W. Yi, T. Kim, T.K. Kim, I.H. Lee, S.R. Paik, T. Hyeon, J. Am. Chem. Soc. 128 (33) (2006) 10658–10659.
[42] T. Hayashi, S. Hirono, M. Tomita, S. Umemura, Nature 381 (1996) 772–774.
[43] V.F. Puntes, K.M. Krishnan, A.P. Alivisatos, Science 291 (2001) 2115–2117.
[44] P. Raveendran, J. Fu, S.L. Wallen, J. Am. Chem. Soc. 125 (46) (2003) 13940–13941.
[45] S. Peng, C. Wang, J. Xie, S.H. Sun, J. Am. Chem. Soc. 128 (33) (2006) 10676–10677.
[46] A.F. Thunemann, D. Schutt, L. Kaufner, U. Pison, H. Mohwald, Langmuir 22 (5) (2006) 2351–2357.
[47] S.K. Batabyal, C. Basu, A.R. Das, G.S. Sanyal, J. Biobased Mater. Bioenergy 1 (1) (2007) 143–147.
[48] F. Durap, M. Zahmakıran, S. Özkar, Appl. Catal., A: Gen. 369 (1–2) (2009) 53–59.
[49] Ö Metin, S. Özkar, Energy Fuels 23 (7) (2009) 3517–3526.
[50] J.-M. Yan, X.-B. Zhang, S. Han, H. Shioyama, Q. Xu, Inorg. Chem. 48 (15) (2009) 7389–7393.
[51] T. Umegaki, J.-M. Yan, X.-B. Zhang, H. Shioyama, N. Kuriyama, Q. Xu, Int. J. Hydrogen Energy 34 (9) (2009) 3816–3822.
[52] Ö Metin, Ş Şahin, S. Özkar, Int. J. Hydrogen Energy 34 (15) (2009) 6304–6413.
[53] F. Durap, M. Zahmakıran, S. Özkar, Int. J. Hydrogen Energy 34 (17) (2009) 7223–7230.
[54] Ö Metin, V. Mazumder, S. Özkar, S. Sun, J. Am. Chem. Soc. 132 (5) (2010) 1468–1469.
[55] Ö Metin, S. Özkar, Int. J. Hydrogen Energy 36 (2) (2011) 1424–1432.
[56] U. Heiz, U. Landman, Nanocatalysis, Springer, Berlin, 2006.
[57] S. Helveg, C. Lopez-Cartes, J. Sehested, P.L. Hansen, B.S. Clausen, J.R. Rostrup-Nielsen, F. Abild-Pedersen, J.K. Norskov, Nature 427 (2004) 426–429.
[58] G.A. Somorjai, D.W. Blakely, Nature 258 (1975) 580–583.
[59] Y. Guo, L. Wang, L. Yang, J. Zhang, L. Jiang, X. Ma, Mater. Lett. 65 (3) (2011) 486–489.
[60] S. Kumer, S. Bai, Indian J. Pure Appl. Phys. 48 (2010) 251–255.